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LEED INVESTIGATIONS OF A CUBIC AL-PD-MN (110) ALLOY

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ABSTRACT

An Al-Pd-Mn cubic alloy having a bulk chemical composition somewhat analogous to that of the icosahedral Al-Pd-Mn quasicrystal is studied. Our goal is to compare the surface structure and properties of the cubic alloy with those of the quasicrystalline alloy. In this paper, we report the first observations for the (110) surface of the cubic alloy using (primarily) low energy electron diffraction (LEED). The surface is prepared by sputtering and annealing in ultrahigh vacuum (UHV). In addition to the substrate LEED pattern, at least three superstructures evolve sequentially with annealing temperature.

INTRODUCTION

In recent years, many investigators have studied quasicrystals because of their unusual surface attributes including their tribological properties, their resistance to oxidation, and their unique surface structures [1,2,3]. It is often desirable to compare the properties of the quasicrystal with those of a crystalline alloy in order to determine which properties are related to chemical composition and which to atomic or electronic structure. To this end, we report here preliminary observations on the surface structure of a cubic (B2) alloy of Al-Pd-Mn. This alloy borders on the icosahedral (i-) region in the phase diagram, and hence it is one of the crystalline analogs closest in chemical composition to the quasicrystalline alloy.

Another reason to study the B2 phase is that it often coexists with the icosahedral phase, e.g. during growth [4]. We have previously shown that Al depletion at the surface of i-Al-Pd-Mn, via preferential sputtering, can also cause the B2 phase to form as a metastable overlayer [4]. This is true for all three high-symmetry surfaces of i-Al-Pd-Mn. For the twofold and fivefold surfaces, the B2 phase exposes a (110) surface which is the same as the surface chosen for this study. Similar observations have been made for other Al-rich quasicrystals [4,5,6,7,8]. In the i-Al-Pd-Mn system, quasicrystalline(-like) LEED patterns can be obtained by annealing to temperatures of 700-900 K.

EXPERIMENT

The sample consists of about six large grains each oriented to within 1° of the [110] axis. The bulk composition of the sample from scanning electron microscopy-energy dispersive x-ray spectroscopy is $Al_{48}Pd_{41}Mn_{11}$. The sample is roughly $15 \times 10 \times 1$ mm^3 in size. It is oriented to within 0.25° of the [110] axis of one of the grains near the center of the sample with Laue x-ray diffraction. It is mechanically polished to a mirror finish with 1 μm diamond paste.

Our UHV chamber is equipped with standard surface analysis equipment including Auger electron spectroscopy (AES) and LEED. The base pressure is 4×10^{-11} Torr or better. Surface preparation of the cubic sample in UHV involves sputtering at room temperature and then annealing. Generally, the sample is sputtered for 17 minutes with Ar^+ ions at normal incidence, 1 keV, and 10 to 12 μA sample current without bias. The sample is manually rastered during sputtering to ensure that the sputter beam covers most of the sample surface. Initial cleaning of

the sample begins at 450 K and increases in 50 K increments when AES reveals no surface segregation of oxygen or other impurities. Annealing intervals of 30 to 60 minutes are used during the cleaning of the sample, and annealing intervals of 1 hour to 3 hours are used during the LEED experiments. All LEED images are obtained after the sample is cooled with liquid nitrogen to 120 K.

We do not report here quantitative compositions from Auger electron spectroscopy, only qualitative trends. We are in the process of checking the surface compositions with low-energy ion scattering with the goal of obtaining more accurate and surface-specific information than AES can provide.

RESULTS

Mild Annealing Temperature 750 K

The LEED pattern in **Fig. 1a** was taken after annealing at 750 K for 2 hours and with an electron energy of 100 eV. The main spots for the substrate lattice are indexed according to standard (h,k) convention--(0,0), (0,1), (1,0), and (1,1). **Fig. 1b** illustrates this indexing scheme.

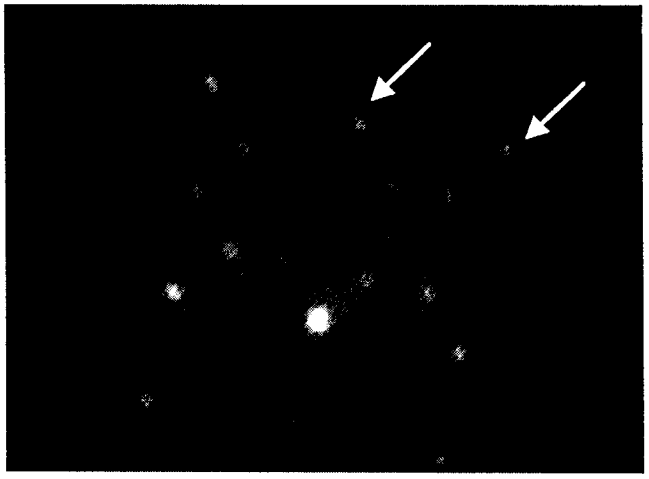

Figure 1a. LEED Pattern at 100 eV incident electron energy and normal incidence after annealing at 750 K for 2 hours. The left and right arrows denote the (0,1) and (1,1) spots, respectively.

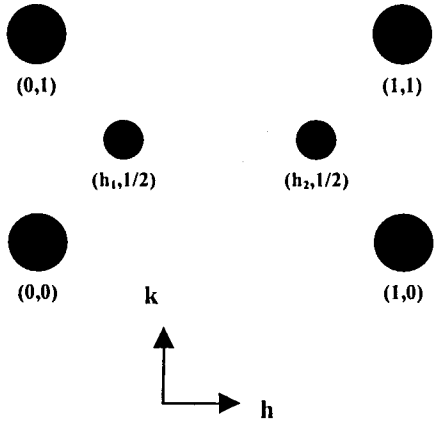

Figure 1b. Indexing scheme for the LEED pattern in Fig. 1a.

The experimental lattice constant, based upon the LEED pattern, is 2.88 ± 0.03 Å. The uncertainty in this measurement expresses the *precision* of five replicate measurements taken from similar LEED patterns. The sample position, with respect to the LEED optics, will tend to influence the *accuracy* of this value, as it is difficult to determine if the sample is exactly at the LEED optics focal point. For comparison, a crystalline β-Al-Pd phase with CsCl structure has a bulk lattice constant of 3.04–3.06 Å [9]. After partial substitution of Mn for Pd, the composition is β-$Al_{48}Pd_{10}Mn_{42}$, and the lattice constant is slightly lower at 3.02 Å [10]. Presumably, our experimental value should lie in between these two, based upon the intermediate Mn content of the bulk sample. Since our value is outside this range, it may reflect the inaccuracy of the LEED measurement.

The LEED pattern in **Fig. 1a** is in sharp contrast to those obtained from the quasicrystalline surfaces of icosahedral Al-Pd-Mn. The spot spacing for the cubic sample is periodic as determined by measuring the spot spacing. There is no evidence of the multiple domains formed by the cubic overlayer on the quasicrystalline surface. Superstructure spots are also visible at k = 1/2. Surprisingly, these spots cannot be indexed to any rational value in the h-direction. At present we are unable to offer an interpretation of the origin of these spots.

AES data for this mildly annealed surface demonstrates Al enrichment relative to the clean surface after sputtering at room temperature. The quasicrystal surfaces also demonstrate this same behavior.

Moderate Annealing Temperature: 800-850 K

Upon subsequent annealing at 800 K to 850 K, the intensity of the half-order spots that first appeared in the LEED pattern at 750 K decreases. An entirely new superstructure develops at these higher annealing temperatures. **Fig. 2a** illustrates the transformed LEED pattern for the cubic sample at an anneal temperature of 800 K and an incident electron energy of 60 eV.

Figure 2a. LEED pattern at 60 eV incident electron energy and normal incidence after annealing at 800 K for 2 hours. The left and right arrows denote the (0,1) and (1,1) spots, respectively.

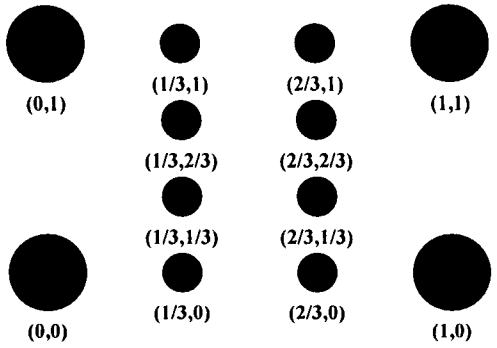

Figure 2b. Indexing scheme for the LEED pattern in Fig. 2a.

Fig. 2b shows the (h,k) indexing scheme for the substrate and the superstructure spots. Note that the superstructure spots in this image are significantly weaker in intensity than both the substrate spots in **Fig. 2a** and the half-order spots in **Fig. 1a**. The AES data at 800 K show a further increase in Al content, relative to the surface formed by annealing to 750 K.

Note that spots at (n, 1/3) and (n, 2/3), where n is an integer, are missing from the image in **Fig. 2a**. We initially speculated that these missing spots were due to a glide plane. A simpler explanation, however, is that the superstructure is due to diffraction from three separate domains, as shown in **Fig. 3**. Each domain consists of rows of pure Al, separated by rows in which pairs of Pd atoms are separated by a Mn atom. Both types of rows are in the [0,0,1] direction. The difference between the domains is in the ordering of the Pd-Mn rows in the [1,-1,0] direction. Note that because of this ordering, the two domains in **Fig. 3a** and **Fig. 3b** are energetically equivalent, but the domain in **Fig. 3c** is slightly different which is somewhat problematic. The

proposed structure results in a surface Pd:Mn ratio of 2:1, which is lower than the bulk ratio of 4:1, although not unreasonable based upon AES data.

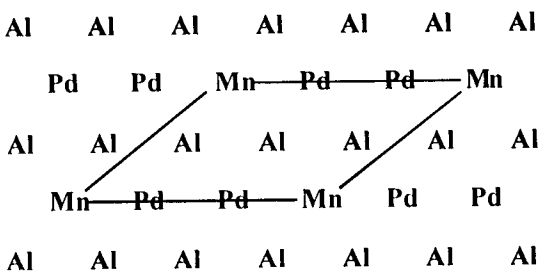

Figure 3a. c (3 × 3) domain #1.

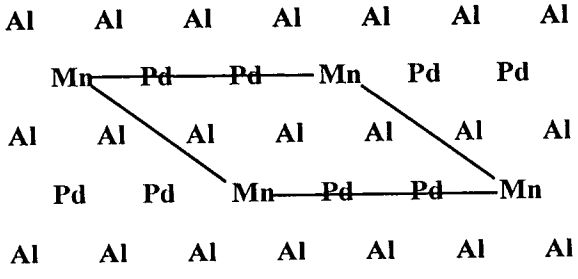

Figure 3b. c (3 × 3) domain #2.

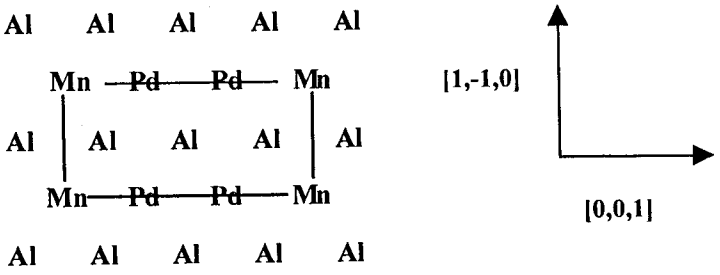

Figure 3c. 1 × 3 domain.

Figure 3. Possible structural model for the cubic Al-Pd-Mn (110) surface. Separations between atoms are shown to scale.

These domains account for the superstructure spots as follows. First, the c(3 × 3) domain in **Fig. 3a** is associated with spots at (1/3, 2/3) and (2/3, 1/3). Similarly, **Fig. 3b** accounts for the spots at (1/3, 1/3) and (2/3, 2/3). Second, the 1 × 3 domain is illustrated in **Fig. 3c** and is associated with spots at positions (1/3, n) and (2/3, n) where n is an integer.

High Annealing Temperature: 900 K

Upon annealing to 900 K, we observe a further transformation in the LEED pattern of the cubic sample. This LEED pattern, at an incident electron energy of 100 eV, is shown in **Fig. 4.** New superstructure spots appear at several locations in the diffraction pattern. For example, half-order spots appear at (1/2,-3/2) and (-1/2,-3/2) but are absent at (1/2,1/2) and other locations. Also, one can barely discern most of the third-order spots that were so evident in the LEED pattern in **Fig. 2a**. Subsequent annealings at 900 K cause increased streaking in the LEED image as is somewhat apparent in **Fig. 4**. In addition, we observe faceting in later LEED patterns at this anneal temperature. Again, the observed LEED pattern is quite complex, and nothing similar to this behavior is observed for the quasicrystal surfaces.

The AES data at 900 K demonstrate an additional increase in the Al content at 900 K, relative to the surface prepared by annealing at 800-850 K.

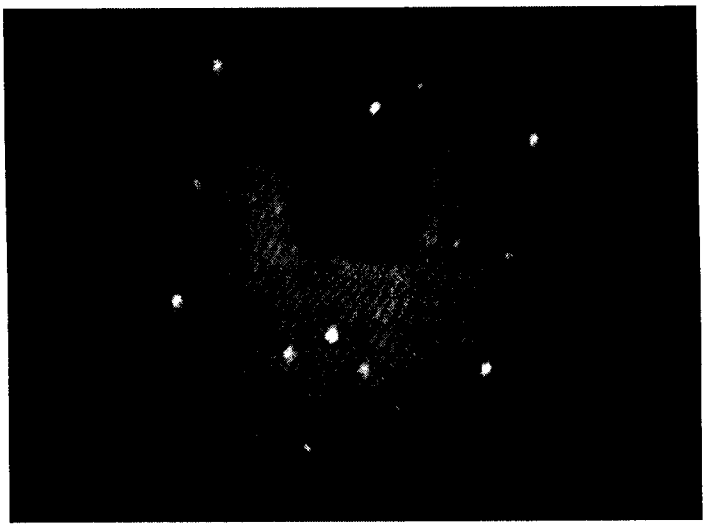

Figure 4. LEED pattern at 100 eV incident electron energy and normal incidence after annealing at 900 K for 2 hours.

CONCLUSION

In summary, we show that the Al-Pd-Mn (110) cubic alloy gives rise to several interesting and complex LEED patterns which depend on the annealing temperature after sputtering. These patterns contrast those we observe for the icosahedral Al-Pd-Mn quasicrystal samples. Annealing the (110) cubic alloy surface causes the Al content at the surface to increase, after preparation by sputtering at room temperature, and this increase corresponds to the transformation of the LEED pattern.

We postulate that a simple model for Pd-Mn ordering on the surface can account for the superstructure that appears in the LEED pattern at 800 K to 850 K. Other patterns appear at lower and higher temperatures for which no model is proposed at this time. The LEED patterns and their interpretations are a continuing subject of investigation in our laboratory.

ACKNOWLEDGEMENTS

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